THE PHOTO-OXIDATION OF BIACETYL AT 4358 Å

by

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VITA

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ABSTRACT

The purpose of this work is to determine whether the quenching of biacetyl phosphorescence by oxygen is due to a chemical reaction between the excited biacetyl and the oxygen, or to a physical quenching process.

In order to determine this, the photolysis of gaseous biacetyl-oxygen mixtures has been studied at 4358 Å and room temperature. The products identified were carbon dioxide, carbon monoxide, water, methanol and formaldehyde. The quantum yields of carbon dioxide and carbon monoxide formation and oxygen consumption were determined.

The carbon dioxide and oxygen quantum yields are independent of absorbed intensity over the range studied, 10^{11}-10^{13} quanta/cm.^{3} second. The carbon monoxide yields may decrease with increasing intensity, but this is not certain because of the large scatter in the yields. The yields increase with oxygen pressure at oxygen pressures less than about 0.1 mm. and reach limiting values at higher oxygen pressures. The variation of carbon dioxide formation and oxygen consumption with oxygen pressure correlates fairly well with the variation of phosphorescence with oxygen pressure.

The significance of this correlation is somewhat doubtful, because of a lack of knowledge of the

secondary reactions in the system. A short chain process
probably predominates.

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I   INTRODUCTION

The photochemistry of biacetyl at 4358 Å has been studied by Sheats and Noyes[82,83] and recently by Noyes, Mulac and Matheson.[66] The luminescence has been studied by many workers (refs. 1-4, 7, 8, 23, 27, 28, 32, 34-37, 39, 43, 44, 47, 51, 53, 57, 59, 68, 69, 76, 85, 92). It has been found that the phosphorescence is quenched strongly by oxygen.[32,47] This study attempts to elucidate the mechanism of the quenching.

A summary of previous work relating to the emission and photochemistry of biacetyl will first be presented. A review of these subjects was published in 1956,[63] therefore we shall concentrate on the later work, giving only a brief summary of work published before 1956.

The Absorption Spectrum of Biacetyl in the Visible and Ultraviolet

The first absorption region of biacetyl extends from 4670 Å to 3500 Å.[36,52] Structure has been detected in this transition down to 4007 Å.[52] This correlates very nicely with the photochemical and luminescence behavior, which also changes between 4047 and 3650 Å. The second absorption region starts at 3200 Å.[86,87]

The Fluorescence and Phosphorescence of Biacetyl

There is disagreement in the literature on the use

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of the terms "fluorescence" and "phosphorescence".
Therefore the definitions used for these terms in this
work will be presented here. Phosphorescence is, in
Pringsheim's[74] words, "a photoluminescence process . . .
involving the passage through a metastable level".
Fluorescence is the light emission which does not
involve the metastable state. When it is desired to
refer to both phosphorescence and fluorescence together,
as on the preceding page, either "luminescence" or
"emission" will be used. The present usage is not
uncommon in this field of research, but it is by no
means universally accepted.

The fluorescence of biacetyl extends from 4400 to
4800 Å. The lifetime of the state from which fluores-
cence occurs, I ^1A_u,[85] is less than 8×10^{-6} second.[32]
The natural lifetime of this state is estimated to be
10^{-5} second. The fluorescence is unaffected by
oxygen.[32,47] The quantum yield of fluorescence is small.

The phosphorescence of biacetyl starts at about
5000 Å and has broad maxima at 5120, 5600 and 6000 Å.[28]
The lifetime of the metastable state, ^3B_g,[85] is $1.8 \times
10^{-3}$ second[1,47,59,76] at room temperature. The quantum
yield of phosphorescence is 0.145 ± 0.03 [4] at room
temperature with 4358 Å excitation. At 3650 Å this
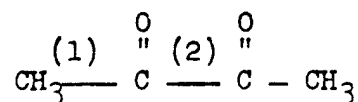yield is reached only at pressures above 30 mm., and

the yield at lower pressure is smaller.

The phosphorescence is strongly quenched by oxygen.[2,3,32,47] Studies of the diminution of lifetime with added oxygen[47] and of the diminution of phosphorescence efficiency with oxygen[3,23] give substantially similar results.

The ratio of phosphorescence to fluorescence is 58:1 at 26°C independent of pressure, exciting wavelength (4358 or 3650 Å) and addition of acetone, benzene or methyl chloride.[68,69] This ratio decreases slowly with increasing temperature in this region and is 30:1 at 84°C.[68] At higher temperature the decrease is more rapid, and at 182°C the ratio is 1.7:1

The Carbon-Carbon Bond Energy in Biacetyl

Of some importance in the understanding of the photochemistry of biacetyl is the amount of energy required to break the bonds (1) and (2).

$$CH_3 \overset{(1)}{\underline{\quad\quad}} \overset{\overset{O}{\|}}{C} \overset{(2)}{\underline{\quad\quad}} \overset{\overset{O}{\|}}{C} - CH_3$$

As a measure of the bond strengths, one could take ΔH for the reactions

1) $CH_3COCOCH_3 = CH_3 + COCOCH_3$

2) $CH_3COCOCH_3 = 2CH_3CO$
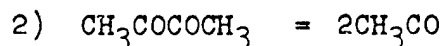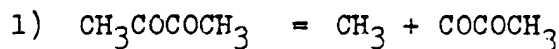
Unfortunately ΔH_1 depends upon ΔH_f (COCOCH$_3$), which is not known, and ΔH_2 depends upon ΔH_f (COCH$_3$), which is the subject of some controversy in the literature.[19]

Calvert[19] has reviewed the data on reaction 3

3) $CH_3CO = CH_3 + CO$
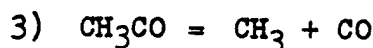
$(\Delta H_3 = E_{a(3)} - E_{a(-3)} = \Delta H_f(CH_3) + \Delta H_f(CO) - \Delta H_f(CH_3CO).$

$\Delta H_f(CH_3)$ and $\Delta H_f(CO)$ are known;[79] $E_{a(-3)} = 3.8$ kcal.[20]), and concludes that "while some information favors the 'high' values [18 ± 1 kcal/mole*] for ...E_3, the majority of the information .... is most consistent with the 'low' estimates [10 kcal/mole*] of these activation energies". Since the review was published, more data have become available favoring the high[35] value, and also the low value.[20]

As Calvert[19] has pointed out, the "high" value implies a CH$_3$CO—COCH$_3$ bond-dissociation energy of 59 kcal/mole, and the "low" value implies 75 kcal/mole. (ΔH_f(CH$_3$COCOCH$_3$) gas = -77.8 kcal/mole[62,89]). Reed and Brand[77] find D(CH$_3$CO - COCH$_3$) ≤ 56.9 kcal by an electron impact method.

The data still do not permit a definite decision between the high and the low values.

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* Values in parentheses are not in the quotation.

There is no point in discussing the strength of the bond CH_3—$COCOCH_3$ here, as no data are available concerning this quantity.

The Photochemistry of Biacetyl

Even if $D(CH_3CO$—$COCH_3)$ is as high as 75 kcal/mole radiation of 3800 Å or shorter wavelength would be sufficiently energetic to break this bond.

At 3650 Å at room temperature, the primary process is

4) $CH_3COCOCH_3 = 2(1-\alpha)CH_3CO + 2\alpha CH_3 + 2\alpha CO$
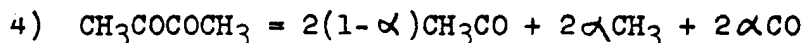
where α is about 0.2 at low pressure and nearly 0.5 at high pressure.[63] The primary quantum yield is small and decreases with increasing biacetyl pressure.

At 4358 Å and room temperature, the primary process is*[66,82,83]

5) $2^3B = B + 2(1-\alpha)CH_3CO + 2\alpha CH_3 + 2\alpha CO$
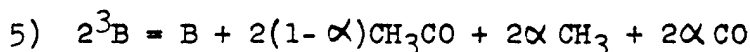
where $\alpha = 0.5$.[63] The primary yield is small and proportional to intensity. At their higher intensities, 3×10^{14} quanta/cm^{3}sec, Sheats and Noyes[82] find $\phi_{CO} = 0.02$, $\phi_{C_2H_6} = 0.005$, $\phi_{CH_4} = 0.0004$.

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* The following symbols will be used often in this work:

B = biacetyl, especially biacetyl in its ground electronic state

^3B = biacetyl in its lowest triplet state

^1B = biacetyl in its first excited singlet state

At temperatures above about 70°C, the decomposition of biacetyl at 4358 Å is first order in the excited species.[66] Under these conditions the triplet state dissociates unimolecularly with an activation energy of about 15 kcal.

At 3130 Å and at shorter wavelengths, the photolysis involves the second excited singlet.[12,14,15] It is therefore not of direct relevance to the present work and will not be treated here. However a knowledge of the primary quantum yield at 3130 Å is useful for comparison with the product yields in Taylor-Blacet's[96] work, discussed in the following section. The primary yield is[63] 0.08 at room temperature, 0.15 at 65°, 0.21 at 100° and 0.22 at 150°C at 3130 Å.

The Photo-oxidation of Biacetyl

Almy, Fuller and Kinzer[2,3] observed that oxygen was consumed when biacetyl-oxygen mixtures were illuminated.

Haagen-Smit, Bradley and Fox[33] found that photolysis of biacetyl in moist air resulted in ozone formation. They found that, with initial biacetyl concentration of 2000 ppm. (about 1 mm. Hg) in air, the ozone concentration reached a maximum of 30 ppm. before declining. They note that no ozone was detected when dry air was used instead of moist air.

Taylor and Blacet[96] studied the oxidation of

biacetyl by molecular oxygen at 3130 Å. The oxygen pressures used were 50-125 mm. (except for one run with oxygen pressure 10 mm.), the biacetyl pressure $\sim$ 100 mm., intensity 3-7 x 10^{12} quanta/cm^3sec and temperatures 60-140°C. The major products found were carbon monoxide, carbon dioxide, formaldehyde and water, with lesser amounts of methanol and acetic acid. They found that the yields depended on the conditioning of the cell wall.

Two series of runs were made with the cell walls cleaned and conditioned by prolonged photo-oxidation at the start of each series. Results of similar experiments generally agreed to within 20% within each series, but the agreement between the two series was not this good. A third series of runs was made with a thin film of boric acid deposited on the cell wall. In this series at 140°C the CO_2 yield was quite reproducible at 1.68 $\pm$ 0.02, but the formaldehyde and carbon monoxide yields were not.

At 60°C the mean values of the carbon dioxide and formaldehyde yields (averaged from Table I of ref. 96) are 0.72 and 0.33, respectively. The carbon monoxide quantum yields very generally from 0.1 to 0.3, and the methanol yields from 0.02 to 0.10. The water yields, in the two runs for which this quantity was measured, were 0.38 and 0.94.

Taylor and Blacet found, in experiments in which the molecular oxygen contained 12% $O^{16}O^{18}$, that the carbon dioxide contained almost exactly one oxygen atom from the molecular oxygen and one from the biacetyl. The carbon monoxide is found to come exclusively from the carbonyl group of the biacetyl. The oxygen in the methanol and formaldehyde come from the molecular oxygen.

Taylor and Blacet[96] propose the following mechanism to account for the products.

1) $CH_3COCOCH_3 = CH_3 + COCOCH_3$

1a) $ = CH_3 + CO + COCH_3$

2) $CH_3COCOCH_3 = 2CH_3CO$

3) $CH_3CO = CH_3 + CO$

6) $CH_3CO + O_2 = CH_3O + CO_2$

7) $ = CH_3O_2 + CO$

8) $CH_3O + O_2 = CH_3 + O_3$

9) $ = CH_2O + HO_2$

10) $CH_3 + O_2 = CH_3O_2$

11) $CH_3O_2 = CH_2O + OH$

12) $CH_3O_2 + O_2 = CH_3O + O_3$

13) $OH + CH_3COCOCH_3 = CH_3COOH + CH_3CO$

14) $ = H_2O + CH_2COCOCH_3$

15) $CH_2COCOCH_3 + O_2 = CH_2O + CO_2 + CH_3CO$

16) $CH_3 + OH = CH_3OH$

17) $CH_3CO + OH = CH_3COOH$

18) $OH + X + wall = Y$

Step 8 is endothermic by at least 60 kcal/mole
($\Delta H_f(O_2) = 0.0$;[79] $\Delta H_f(O_3) = 34.0$;[79] $\Delta H_f(CH_3) = 32.0$;[79] $\Delta H_f(CH_3O) \sim -0.5$ [31]) and will therefore be disregarded in the present work.

The mechanism proposed by Taylor and Blacet is a chain mechanism. The hydroxyl radical is the chain carrier. If the primary dissociation yield in the presence of oxygen is equal to the primary yield in the absence of oxygen (~ 0.14 at 60° [63]), then for each primary dissociation, five molecules of carbon dioxide and about one of carbon monoxide are formed. With biacetyl-iodine mixtures, the primary quantum yield is somewhat lower than the primary yield for pure biacetyl.[12] Oxygen and iodine probably have similar effects on the primary yield. If this is so, then for each biacetyl molecule which is destroyed in the primary process more than five molecules of carbon dioxide are formed.

G. B. Porter[41,73] has made a study of the photo-oxidation of biacetyl at 4358 Å at 30°C. He also found considerable unreproducibility in the quantum yields. The yields of oxygen uptake were 1.2-2.3, $\Phi(CO_2) = 0.95-1.49$, $\Phi(CO) = 0.15-0.34$, $\Phi(CH_3OH) = 0.13$ for the one run in which CH_3OH was determined. Formaldehyde, acetone, acetaldehyde and some high-molecular-weight substances were also found.

Stevens and Dubois have found that oxygen is consumed when biacetyl-oxygen mixtures in aqueous solution are exposed to light of 4358 Å.[92]

II EXPERIMENTAL

Apparatus

The vacuum line used was similar to that used in most investigations in this laboratory.[36] It consisted of a storage section, connected to the cell system, which was in turn connected to the analytical system.

The storage system (see Fig. I) consisted of a manifold, to which were connected: a 12/30 female standard taper-ground joint and a high-vacuum stopcock behind cutoff A, for introducing biacetyl; storage bulbs behind cutoffs B and C, for distilling and storing the biacetyl; a cutoff D, connected to the high-vacuum manifold, for evacuating the storage system; a small doser (Toepler) E, for introducing oxygen; and a McLeod gauge at H for measuring oxygen pressure. The cell was connected through a cutoff at G. Since the mercury in cutoff A was raised except when introducing biacetyl for storage, or during some early, probing runs, while removing biacetyl or products, this was usually a stopcock and grease-free system. However, after Run 79 a bulb of oxygen-18 (not shown on diagram) was attached behind two stopcocks in series, directly to the supply manifold. The two stopcocks and the space between them were used as a doser for oxygen-18.

The two storage bulbs were pear-shaped, of about 10

Figure I

Storage System and Cell

High Vacuum Manifold

Supply
Manifold
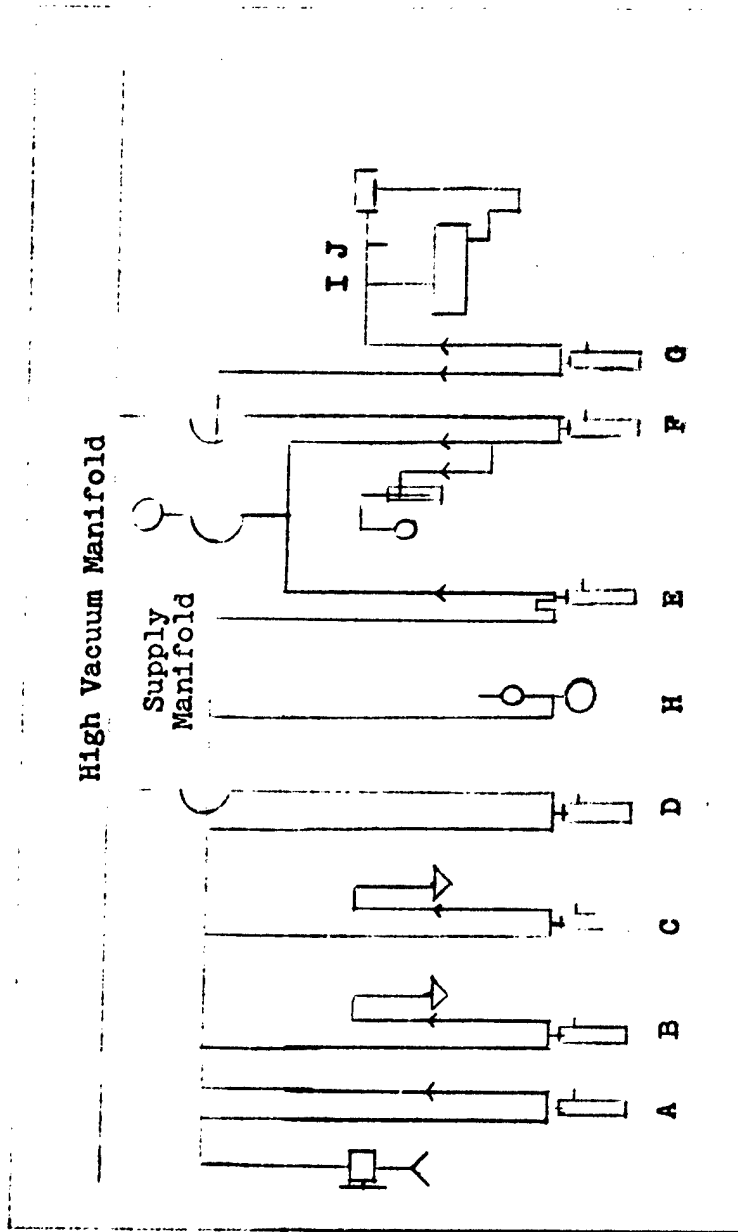
ml. capacity. The tubing leading to these bulbs was
painted outside with black Glyptal to keep out light.
On the portion of the tube immersed in the dry-ice-
acetone mixture, the Glyptal did not adhere. Therefore
whenever biacetyl was stored in one of the bulbs, the top
of the Dewar containing the dry-ice-acetone mixture was
covered with black paper, as is used to cover photo-
graphic plates. The bulbs were protected with float
valves, as shown in the diagram, so that if air should
be admitted, intentionally or otherwise, to the line,
the air could be kept out of the biacetyl supply.

Similarly, the purpose of the float valve shown on
the manifold side of cutoff A was to protect the bulk of
the line in case the stopcock were to leak.

The two tubes leading to cutoff D were aligned ver-
tically with considerable care, and used as a mercury
manometer to measure biacetyl pressure. These tubes were
of 8-mm. Pyrex tubing, as was most of the line.

The oxygen generating and storage system is des-
cribed below, under Preparation of Materials. The doser
was merely a small Toepler pump by which one could intro-
duce small amounts of oxygen into the supply manifold
and cell. It was observed that with a pressure of oxygen
of 10 mm. in the storage bulb, one dose was equivalent
to a pressure of 0.003 mm. in the cell and storage

system. Owing to the small volume of the doser, and the comparatively large area at the cutoff point, great reproducibility could not be expected from this figure. Therefore, the pressure of oxygen was always measured before the run on the McLeod gauge or the manometer.

Up to and including Run 56, readings of oxygen pressure were taken on the same McLeod gauge which was used to determine products. It was finally decided at this point that this procedure, with its necessity for pumping the oxygen out of the analytical section between the start of the run and the analysis of products, was too time-consuming. Therefore a McLeod gauge was built into the supply section as shown at H on the diagram. This gauge had a volume of 280.5 cm^3, determined by weighing the amount of water required to fill it. It was fitted with Fisher and Porter precision bore capillary of 0.0315 inch (0.8001 mm.) inside diameter. The length of capillary was slightly under 300 mm. Thus the useful range of the gauge was up to about 0.180 mm.

The supply manifold was connected by means of a short cutoff, G, with float valves to the cell.

The gases in the cell could be circulated and mixed by means of a stirrer. The gas would flow from the cell, through a U-tube cold trap, through the stirrer, back to the cell. The short cutoffs, at I and J, leading to the

supply system and the analytical system, were attached between the stirrer and cell. The stirrer and tubing were painted with black Glyptal, and a black curtain was placed between the light source and most of the tubing. The volume of this system between the two cutoffs was 316 cm^3.

The cell itself was cylindrical; made of quartz, 20 cm. long and 2.8 cm. in diameter (outside dimensions). Its internal volume was 86 cm^3. It was encased in an aluminum block furnace, whose edges extended 3 cm. beyond the ends of the cell. The furnace was in turn wrapped with asbestos paper, heating wire, and more asbestos paper. It was provided with a well for a thermometer, whose readings are recorded as the cell temperature.

The light source, filters and phototube are described below.

The analytical section consisted of a series of cold traps, A, B, C and D in Fig. II, for separating the various fractions, a ground glass joint, G, for removal of condensable products, a Toepler-McLeod gauge, E, and a copper-copper oxide furnace, F, for the analysis of the non-condensable fraction. After Run 79, another Toepler pump was added to enable removal of the non-condensables from the line, in order to analyze these on the mass spectrometer.

Figure II

Analytical System

High Vacuum Manifold
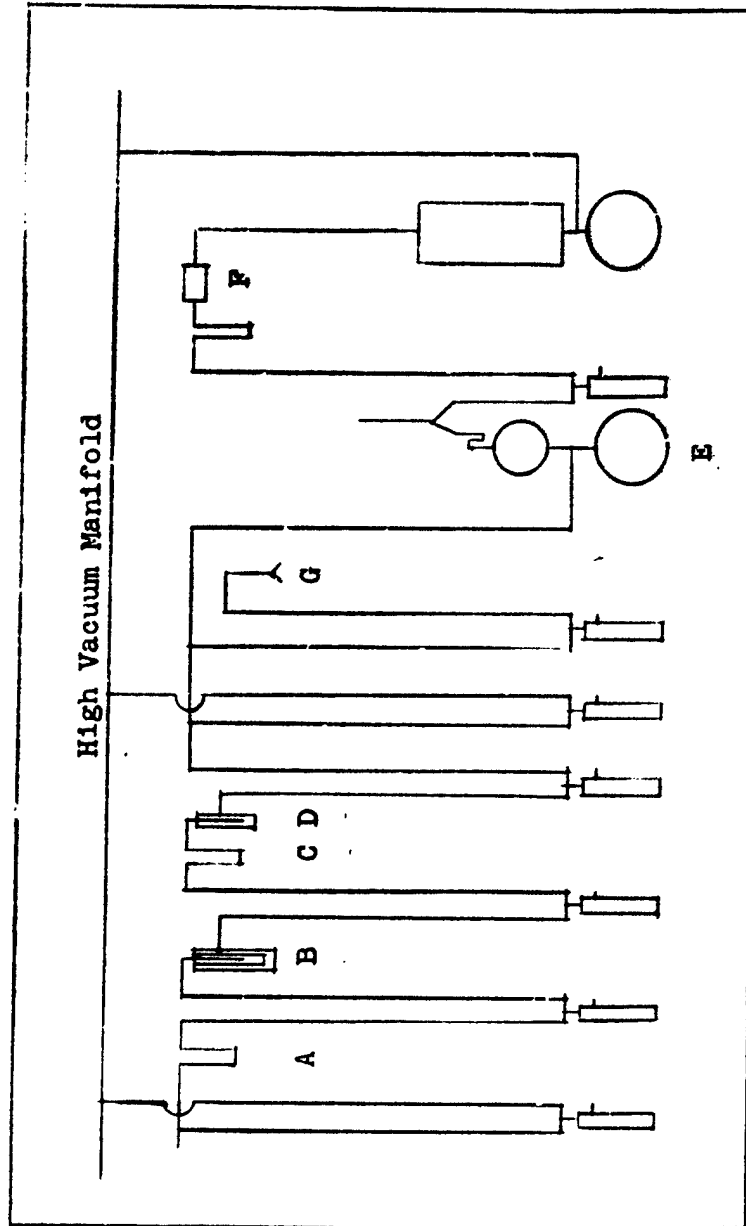
The traps were, in order proceeding from the cell to the Toepler-McLeod: a U-tube, a variable-temperature still, after Leroy,[50] another U-tube, and a ring-seal trap. Their use is described in the section <u>Description of a Run.</u>

The Toepler-McLeod was of the Strachan[93] design. Thus the non-condensables, after being measured, could easily be expanded into the furnace.

The furnace consisted of a piece of 10-mm. glass tubing filled with short pieces of copper wire, and surrounded by an aluminum block. The heating arrangements were similar to those described for the cell. Since the gas analyzed was mostly oxygen, the furnace occasionally had to be reconditioned by use of CO as the reducing gas. To the furnace were attached a U-tube cold trap, which was kept in liquid nitrogen during operation and reconditioning of the furnace, and a large bulb in which mercury could be raised or lowered. When the mercury was completely lowered, the furnace was connected to the high-vacuum manifold, and could be evacuated. When it was partially lowered, the large dead space, about 300 cm^3, permitted most of the gas from the McLeod to expand into the furnace area.

The light source was a medium-pressure mercury arc, the Hanovia Type S-100 Quartz Alpine Sun Burner. The

light was collimated with a quartz lens of short focal length and passed through a Corning CS-5-74 glass filter. In the runs at reduced intensity, copper wire screens were interposed between the filter and the cell. One layer of screen removed approximately 2/3 of the light. The cell has been described. After passing through the cell, the light was focused, using a quartz lens, on an RCA Type 929 phototube, whose output was measured on a Varian type G-10 recorder.

Preparation of Materials

Biacetyl, Eastman white label, was kept overnight in the dark, under a rough vacuum, over Drierite. The container of biacetyl was then attached to the ground glass taper joint at the supply system of the vacuum line, the biacetyl frozen out at dry-ice temperature, and pumped on for about one hour. It was then immersed in an ice-water bath, and permitted to warm to $0°C$, after which it was distilled into one of the storage bulbs, with a first and last fraction being discarded. The middle fraction was degassed for about one hour at dry-ice temperature, and then distilled into the other bulb, again discarding the end fractions. Thus, of a 10-ml. sample of biacetyl which was used at the start, only 1-2 ml. were retained. This fraction was then degassed overnight. The whole process was carried out in the dark.

It seems pertinent to include two remarks on the process here: first, on two occasions, a large amount of the biacetyl polymerized over the drying agent (this was shown in an increase in the viscosity of the liquid, a decrease in vapor pressure, and on one occasion, by crystallization of the residue after distillation); and secondly, in degassing biacetyl at dry-ice temperature, a small amount of biacetyl itself is pumped off. (Okabe (ref. thesis) has estimated the vapor pressure of biacetyl at -78°C as 0.1).

The purity of the biacetyl was then checked on the Vapor Fractometer. It was found that some water remained in the biacetyl. Attempts to remove the water by using more vigorous drying were successful, but resulted in considerable decomposition of the biacetyl. Damp biacetyl was therefore used as the lesser evil. If total impurities other than water exceeded 0.5%, the sample was discarded. Methyl ethyl ketone was the major impurity besides water.

Oxygen was prepared in the vacuum line, by heating potassium permanganate, and purified by passing through a trap at liquid nitrogen temperature. It was stored in a three-liter bulb, whence it could be dosed into the supply manifold.

Oxygen-18 was obtained from the Weizmann Institute.

Their stated analysis of the sample used is: 97.604% O^{18}, 0.301% O^{17}.

Description of a Run

The biacetyl storage bulb was warmed to a temperature below room temperature and biacetyl vapor permitted to fill the supply manifold and cell system. The pressure was read on the supply system manometer. Then the cutoff between the cell and supply manifold was raised, the biacetyl in the storage manifold condensed back into the bulb at $-78°C$, and that in the cell condensed into the U-tube at the melting point of ethyl ether, $-120°C$. The supply manifold was pumped on for 10-15 minutes, the cutoff to the cell was lowered and the biacetyl in the U-tube degassed for 1/2 hour. At the beginning of this half-hour, the lamp was turned on, with the cell shielded from its light, in order to give it time to equilibrate. If, at the end of this half-hour any pressure was detected on the McLeod, the degassing process was continued until a vacuum was obtained. Then the oxygen was dosed in and its pressure measured. The intensity of the light traversing the cell with the biacetyl still frozen out was measured. The cell was again shielded from the light, and the cutoff raised. The ether trap was replaced with warm water to volatilize the biacetyl rapidly.

The biacetyl and oxygen were mixed for 20-30 minutes

before the illumination was started. The intensity of
light at the phototube was measured at intervals through-
out the run. After the run, the biacetyl was frozen
into the U-tube at -78°C, and the light intensity again
measured. The cell was then opened to the first U-tube
trap in the analytical section, and the dry-ice-acetone
(or ether) mixture removed from the cell U-tube and
placed on the other one. The purpose of this first trap
was to hold back the greater part of the biacetyl where
it would not interfere with the analysis for the more
volatile components. The uncondensed gases were per-
mitted, after 15-20 minutes, to expand into the Leroy
still, which was at liquid nitrogen temperature at this
point. One half-hour was allowed for equilibration here,
then the gases were expanded into the rest of the analyt-
ical section. The last trap was usually immersed in
liquid nitrogen at this time to insure the trapping of
all condensable materials. (For several early runs,
solid nitrogen was used, in the hope of separating an
ethane fraction. Since no ethane was found, this was
discontinued.) The non-condensables were then trans-
ferred by the Toepler pump into the McLeod gauge and
measured. This fraction was then expanded into the
copper-copper oxide furnace and allowed to react for at
least two hours. The U-tube at the furnace was immersed

in liquid nitrogen throughout this time. While the non-condensables were reacting in the furnace, the carbon dioxide fraction was vaporized and measured. The cutoff between the first U-tube and the Leroy still was raised, and the temperature of the Leroy still raised to -130°C. Thus the carbon dioxide distilled from the Leroy still into the last trap, which was still surrounded by liquid nitrogen. After no less than 40 minutes, the cutoff between the still and the last trap was raised, and the liquid nitrogen removed from the last trap. The gas thus obtained, which was shown by mass spectrometric analysis to be carbon dioxide, was transferred to the McLeod and measured. It was then usually pumped out of the line, except in the early runs when its identity was being determined, and in the oxygen-18 experiments. When a vacuum was obtained again in the McLeod section, the mercury in the McLeod gauge was raised. If the time for measuring the products from the copper-copper oxide furnace had come, this was done as described below; in any event the mercury was left in the raised position during the next step to keep the biacetyl out of the gauge. All the traps in the analytical section were permitted to warm to room temperature, and the biacetyl and remaining products distilled into a takeoff tube which was attached at the ground joint, and was kept at liquid nitrogen

temperature. This was then removed to the vapor fractometer, mass spectrometer, infrared spectrometer, or other means of analysis.

A description of the results of analysis of the "liquid fraction" is given below. Gases from the copper-copper oxide furnace volatile at liquid nitrogen temperature were determined as methane, then the liquid nitrogen trap was replaced by a dry-ice-acetone trap, and the carbon dioxide, which had arisen by oxidation of the original carbon monoxide, was determined. Oxygen remaining after the run was calculated by subtraction of the methane plus carbon monoxide from total non-condensables. Oxygen consumed was calculated by difference.

Actinometry

The actual absorbed intensity was calculated by using biacetyl, photolyzed at room temperature at 4358 Å as an actinometer. The quantum yields for this system have been measured by Sheats and Noyes.[82] These quantum yields are proportional to the intensity. From the values given in Table I of Ref. 82, one obtains:

1) $I_a = 1.3 \times 10^{16} \, \Phi_{CO}$ quanta/cm^3 second

2) $I_a = 1.1 \times 10^{16} \, (\Phi_{CO} + \Phi_{CH_4} + \Phi_{C_2H_6})$,

at 4358 Å and $28 \pm 3°C$. Since $\Phi_{CO} = [CO]/I_a t$,

3) $I_a^2 \simeq 1.3 \times 10^{16}$ $[CO]/t$

4) $I_a^2 = 1.1 \times 10^{16}([CO] + [CH_4] + [C_2H_6])/t.$

In the expressions above, $[CO]$, $[CH_4]$ and $[C_2H_6]$ are the concentrations of products in molecules/cm^3 of irradiated volume. The irradiated volume was taken as 86 cm^3.

By this method I_a is found to be 1.4×10^{13} quanta/ cm^3 second at the highest intensity generally used. The cm^3 in the denominator refers to the irradiated volume. This estimate of I_a is probably accurate to within at best a factor of two. I_a at the lower intensities is estimated by assuming that the recorder output is linear with intensity.[36]

Attempted Analysis of the Liquid Fraction

A quantitative analysis of the liquid fraction was never accomplished. In fact, considerations of mass balance cause one to doubt that a complete qualitative analysis was obtained. The three products in this fraction whose presence was fairly certain were methanol, formaldehyde and water, and the evidence for their presence is presented here.

Methanol: Peaks at m/e 31 and 32 on the mass spectrogram of the liquid fraction imply the presence of methanol. These peaks appear at m/e 33 and 34 in the oxygen-18 experiments. Also, with the use of a four-

meter column of Carbowax methoxypolyethylene glycol 350
on firebrick, a peak was detected in the reaction products
which was not present in the starting material; and the
retention time of this peak corresponded well with that
of methanol. With the other columns used, the methanol
peak would be expected to be hidden by either the biace-
tyl peak or the water peak, and therefore undetectable.

Formaldehyde: Formaldehyde was detected among the
liquid products by use of Matsukawa's[58] test, as des-
cribed in Mueller's[61] dissertation. First the liquid
fraction was dissolved in water, then the biacetyl was
precipitated out as the semicarbazide, then the mixture
was centrifuged and the supernatant liquid decanted.
The test was run on the supernatant liquid. The red
color, indicating formaldehyde, was quite pronounced.
Unfortunately, the solution was somewhat turbid, and
quantitative measurements could not be made. Formalde-
hyde was never detected in the liquid fraction by vapor
chromotography, but it was not detected in formaldehyde-
containing blanks by this method either.

Water was a suspected product, but since it was
present in the starting material, no evidence either for
or against its formation was found until the runs with
oxygen-18. Here mass spectra showed the presence of some
water-oxygen-18 (peaks at m/e 19 and 20).

Infrared analyses, using a Perkin-Elmer model 21
spectrophotometer, were fruitless, because of the small
amounts of materials used. An attempt was made to con-
vert any aldehydes and ketones in the liquid fraction to
the 2,4-dinitrophenylhydrazones, and to separate these by
paper chromatography, but biacetyl was the only material
thus detected.

III   RESULTS

The products detected during photolysis of biace-
tyl-oxygen mixtures were carbon monoxide, carbon dioxide,
small amounts of methane, methanol, formaldehyde and
water. Ethane was absent. Quantitative data were
obtained for carbon monoxide, carbon dioxide, methane,
and oxygen uptake. The last two would be expected, a
priori, to be less accurate than the first, because in
the case of methane only small amounts were produced, and
in the case of oxygen, the uptake is the small difference
between two large figures. It was actually found that
the results for carbon monoxide and carbon dioxide were
not very reproducible, also.

The rates of formation of products, and of disap-
pearance of oxygen, are given in Table I. The rates are
presented as measured, in mm./hour in the cell volume
(316 cm^3) at room temperature. These Rp values are
proportional to the quantum yields at each intensity
used, to within about 10%. The inaccuracy is introduced
by the day-to-day fluctuations in the output of the
light source.

For those runs in which the intensity was monitored,
the quantum yields are given in Table II. The absolute
accuracy of these figures is not great. They are pre-
sented to two significant figures merely to facilitate

comparison among the different values in this table. These yields were calculated on the basis of irradiated volume, 86 cm^3, rather than total volume.

In addition, the relative amounts of carbon dioxide-$O^{16}O^{16}$, carbon dioxide-$O^{16}O^{18}$ produced in the runs with oxygen-18 were measured. These data are presented in Table III.

TABLE I

Product Yields in the Photo-oxidation of Biacetyl

$$I_a \simeq 10^{13} \text{ quanta/cm}^3\text{second}$$

Run #	Temp. °C	P_B mm.	Duration sec.	P_{O_2} Init. mm.	P_{O_2} Final mm.	P_{O_2} Mean	Yields mm./hr. x 10^3 CO	ΔO_2	CO_2	CH_4
12	26	25	7200	.426	.243	.360	24.4	66.3	90.1	0.1
13		11	5760	-	-	-	10.9	-	12.7	0.2
15		10	3840	.228	.217	.223	4.4	10.2	78.6	0.3
16	28	21.2	3600	.141	.075	.118	12.2	46.2	-	0.2
17	26	20	3600	.259	.235	.247	0.1	24.0	-	0.2
18	31	17	2880	.173	.144	.159	2.2	35.6	5.8	0.1
19	30	25	3600	.172	.181	.177	0.1	-	60.2	0.2
20	31	25	2160	.110	.131	.120	23.7	-	68.6	0.2
21	31	16	3672	.268	.198	.233	18.2	69.4	54.4	0.1
22	30	24.5	3600	.318	.223	.271	0.0	95.2	26.8	0.1
25	26	23.7	3600	.622	.421	.522	21.1	201.0	74.8	74.8
27	23.5	21	1800	.199	.168	.183	0.0	62.6	55.0	0.1
28	25	19	1800	.197	.157*	.177*	16.2	80.2*	49.6	0.1

* These figures based on assumed R_{pCH_4} of 0.2 x 10^{-3} mm./hr.

TABLE I (cont'd) $I_a \cong 10^{13}$ quanta/cm³second

Run	Temp.	P_B	Duration	P_{O_2} Init.	Final	Mean	Yields mm./hr. x 10³ CO	ΔO_2	CO_2	CH_4
29	27	25	900	.240	.214	.227	17.0	105.6	71.2	0.0
30	30	24.5	2160	.128	.088	.108	16.4	66.8	52.5	0.3
31	30	20	900	.111	.097	.104	12.4	56.8	50.4	0.0
32	27	24	900	.149	.122	.135	18.4	107.2	72.0	0.0
33	24	20	900	.092	.071	.082	16.2	82.0	60.0	0.0
34	26	21	900	.148	.119	.134	16.0	126.0	68.0	0.0
37	27	23	374	.171	.151	.161	24.2	192.3	88.8	0.0
38	24	27	900	.134	.109	.121	17.0	96.8	76.0	0.0
39	24	19	900†	.220	.193	.206	17.0	106.4	70.8	0.0

† Three 300-second exposures separated by 1200-second dark periods

| 40‡ | 24 | 20.5 | 360 | .122 | .125 | .123 | 24.1 | - | 7.1 | 0.0 |

‡ The biacetyl was photo-oxidized for 8113 sec., then degassed and used in this run.

41	24	22	600	.171	.151	.161	16.6	120.0	69.0	0
42	26	25.5	900	.098	.074	.086	15.4	96.4	58.4	0
47	25	20.5	600	.099	.083	.091	24.6	96.6	52.8	

TABLE I (cont'd) $I_a \cong 10^{13}$ quanta/cm^3second

Run	Temp.	P_p	Duration	P_{O_2} Init.	Final	Mean	Yields mm./hr. x 10^3 CO	ΔO_2	CO_2	CH_4
48	24	18.5	600	.202	.179	.191	18.6	136.8	77.4	0
49	25	21.	600	.072	.057	.065	17.4	88.2	31.2	0.1
50	27	23	600	.063	.046	.054	21.5	79.6	66.6	0.9
51	27	24	600	.101	.081*	.091*	-	121.2*	77.6	-

* based on assumed CH_4 + CO yields of 21.5 x 10^{-3} mm./hr.

Run	Temp.	P_p	Duration	P_{O_2} Init.	Final	Mean	CO	ΔO_2	CO_2	CH_4
52	29	27	360	.040	.006	.023	5.3	336.	57.0	270.
53	29	24	900	.034	.022	.028	5.1	45.4	27.2	0.1
55	30	38	18,420	.000	.000	.000	CO + CH_4 = 0.73 x 10^{-3} mm./hr.			
59	23	24.4	3720	.074	.051	.062	1.0	21.5	24.7	0.04
64**	89	13.2	300	.073	.075	.074	0.2	-	6.2	1.2

** Pressures and R values measured at 28°

$I_a \sim \frac{1}{3} \times 10^{13}$

Run	Temp.	P_p	Duration	P_{O_2} Init.	Final	Mean	CO	ΔO_2	CO_2	CH_4
35	27	24	1800	.179	.149	.164	7.2	59.0	26.2	0.0
36	27	18	2160	.165	.140	.153	5.8	42.0	18.8	0.0
43	25	20.5	1200	.045	.037	.041	4.4	23.4	12.2	0.1
44	25	20.2	2400	.051	.037	.044	5.4	20.7	14.5	0
45	25	20.3	1200	.105	.095	.100	4.0	29.7	18.0	0.5
46	24	21.0	1800	.045	.034	.039	0	23.6	18.8	3.4

TABLE I (cont'd)

$I_a \sim 10^{12}$

Run	Temp.	P_B	Duration	P_{O_2} Init.	Final	Mean	Yields mm./hr. x 10^3 CO	ΔO_2	CO_2	CH_4
54	29	26	9000	.069	.046	.057	1.10	9.12	5.20	0.01
67	24	24	11,700	.075	.060	.067	0.1	4.6	4.6	0.0
68	24	25	11,700	.067	.048	.058	3.12	6.0	5.1	0.1
69	24	37	11,700	.097	.070	.084	5.18	8.4	6.6	0.18
70	29	24	12,015	.072	.055	.064	1.54	5.1	4.7	0.18
73	23	24	5400	.091	.082	.087	2.63	6.3	5.5	0.21

$I_a \sim 2 \times 10^{11}$

Run	Temp.	P_B	Duration	P_{O_2} Init.	Final	Mean	CO	ΔO_2	CO_2	CH_4
71	27	26	46,800	.089	.072	.081	0.35	1.32	0.87	0.02
72	23	23	9900	.088	.087	.088	0.43	0.49	0.85	0.06
74	24	20	36,900	.079	.069	.074	0.59	0.96	0.72	0.03

TABLE II
Quantum Yields

Run #	T °C	P_B mm.	I_a x 10^{-12}	Duration min.	P_{O_2} mm.	Φ_{CO}	Φ_{O_2}	Φ_{CO_2}
29	27	25	20	15	0.227	.029	0.17	0.12
30	30	24.5	18	36	0.108	.028	0.12	0.10
31	30	20	16	15	0.104	.025	0.12	0.10
32	27	24	17	15	0.135	.035	0.21	0.14
33	24	20	16	15	0.082	.033	0.17	0.12
34	26	21	17	15	0.134	.031	0.24	0.13
35	27	24	5.7	30	0.164	.042	0.34	0.15
67	24	24	0.93	195	0.068	.003	0.16	0.16
68	24	25	1.15	195	0.058	.089	0.17	0.15
69	24	37	0.97	195	0.084	.18	0.29	0.22
70	29	24	0.81	200.25	0.064	.062	0.21	0.19
71	27	26	0.20	780	0.081	.055	0.22	0.14
86	26	17	8.5	15	0.7			0.20
87	26	22	10.5	15	1.0			0.33
90	24	13	8.5	15	1.0			0.33
91	25	13	8.3	132	0.9			0.19
93	26	12.5	8.1	30	0.9			0.23
94	25	12	9.4	15	0.4			0.24
97	31	13	3.8	45	1.0			0.28
106	28	12	7.8	60	0.9			0.21
110	27	18.5	8.0	30	2.1			0.24
111	-	18.7	8.1	30	1.0			0.18
113	25	17.9	8.1	15	1.8			0.18

TABLE III
Isotopic Composition of CO_2 from Runs with Oxygen-18
t = 27 $\pm$ 2°C

Run #	P_{O_2} mm.	P_B mm.	Duration min.	% CO_2^{16}	% $CO^{16}O^{18}$	% CO_2^{18}
			$I_a = 8 \times 10^{12}$			
99	1.0	13	6	7	54	39
104	0.9	12	6	10	48	42
107	1.0	12.5	7.5	12	52	36
87	1.0	22	15	6	78	16
90	1.0	13	15	7	66	27
94	0.4	13	15	7	70	22
105	1.0	13	30	8	73	19
93	0.9	13	30	7	72	21
82	0.1	13	60	6	78	16
89	1.0	13	60	7	78	15
106	0.9	12	60	5	83	12
91	0.9	13	120	4	88	8
95	0.5	12	120	4	89	7
			$I_a = 4 \times 10^{12}$			
85	0.4	13	186	15	72	13
97	1.0	13	45	7	63	30
100	2.5	17	2376	3	89	8
			$I_a = .46 \times 10^{12}$			
101	1.0	12.5	405	6	73	21
102	1.0	12.5	1601	5	84	11

To within the accuracy of the data, the yields do not vary with biacetyl pressure. There appears to be a trend toward decrease of quantum yields with increasing time of reaction at a given intensity and mean oxygen pressure, but this is by no means certain. The quantum yields of oxygen uptake and of carbon dioxide are independent of absorbed light intensity over the range studied, 2×10^{11} - 2×10^{13} quanta/cm^3 second, while the carbon monoxide yield appears to increase with decreasing intensity. At oxygen pressures greater than about 0.15 mm., the variation of yields with oxygen pressure is small, but the yields fall off considerably at lower oxygen pressure.

By the method of least squares, the relation between mean oxygen pressure during a run and the product yields was found. The data for the 900-second runs, numbers 29, 31, 32, 33, 34, 38, 39, 42 and 53, and for the 600-second runs, numbers 41, 47, 48, 49 and 51, were used in these calculations. Equations of the following forms were fitted to the data:

$$1) \quad \frac{1}{R_p} = a_1 \frac{1}{P} + b_1$$

$$2) \quad \frac{1}{R_p} = a_2 P + b_2$$

$$3) \quad R_p = a_3 \frac{1}{P} + b_3$$

$$4) \quad R_p = a_4 P + b_4 \, ,$$

where a_1 and b_1 are constants determined by the least-squares fitting, P is the mean pressure of oxygen, and R_p is proportional to the quantum yield.

As a measure of the relative applicability of each equation, the absolute value of the quantity $(R_p{}^c - R_p{}^o/R_p{}^c)$, averaged over all experimental points in a given series, was used. ($R_p{}^o$ is the observed R_p; $R_p{}^c$ is the value calculated by Eqs. (1), (2), (3) or (4). This measure was chosen for three reasons:

(a) It permits direct comparison among the results for the four different equations. In this respect, it is superior to taking $\overline{|1/R_p{}^c - 1/R_p{}^o|}$ or $\overline{(1/R_p{}^c - 1/R_p{}^o)^2}$ for Eqs. (1) and (2), and $\overline{|R_p{}^c - R_p{}^o|}$ or $\overline{(R_p{}^c - R_p{}^o)^2}$ for (3) and (4).

(b) It does not intrinsically favor any one of the equations (1)-(4). The least-squares treatment of Eqs. (1) and (2) finds that set of constants which minimizes $\overline{\left(\frac{1}{R_p{}^c} - \frac{1}{R_p{}^o}\right)^2}$, while the treatment of (3) and (4) minimizes $\overline{(R_p{}^c - R_p{}^o)^2}$. Thus using $\overline{(R_p{}^c - R_p{}^o)^2}$ as a measure of the fit would introduce a factor favoring Eqs. (3) and (4) over (1) and (2). It seemed that $\frac{\Delta R_p}{R_p}$ (ΔR_p is the error in R_p) was the fairest simple measure since, for small $\Delta R_p/R_p$, $\left|\Delta R_p/R_p\right| = \left|\Delta(1/R_p)/\left(\frac{1}{R_p}\right)\right|$.

(c) The reason R_p^c instead of R_p^o was used as the denominator is that R_p^c is the smoother function of P. This choice is still largely arbitrary.

The average values of $\left| \left(R_p^c - R_p^o \right) / R_p^c \right|$, expressed in percent, for each of the twenty-four combinations of product, duration, and equation fitted, are shown below.

Eq.	ΔO_2 15min	ΔO_2 10min	CO_2 15	CO_2 10	CO 15	CO 10
1	12.0%	8.7	8.8	23.0	14.8	11.2
2	26.0	7.0	23.7	22.0	34.8	11.3
3	11.3	9.1	6.4	21.0	7.4	10.8
4	17.7	7.5	14.9	19.2	18.1	10.6

From this table, it appears that the 10-minute (600-second) runs cannot form a basis for choice of one plot over another. For the 15-minute runs, Eqs. (1) and (3) consistently fit the data better than (2) or (4). In the case of carbon monoxide, (3) gives a considerably better fit than (1), but for the oxygen uptake and carbon dioxide yield, the difference is not great.

An objection to Eq. (3) is that the constant a_3 is negative; and a short extrapolation would predict that the yields all become negative when the oxygen pressure is below 0.02 mm. Hg. This extrapolation may not be justified, as the rate-determining steps at very low

oxygen pressures are possibly not the same as at the pressures used here. Therefore the best equations of this form are reproduced, along with those of form (1).

For the 900-second runs:

5) $- \dfrac{1}{R_p(O_2)} = 0.411 \left(\dfrac{1}{P}\right) + 7.43$

6) $- R_p(O_2) = -0.00202 \left(\dfrac{1}{P}\right) + .1142$

7) $\dfrac{1}{R_p(CO_2)} = 0.750 \left(\dfrac{1}{P}\right) + 9.32$

8) $R_p(CO_2) = -0.00148 \left(\dfrac{1}{P}\right) + .0783$

9) $\dfrac{1}{R_p(CO)} = 4.54 \left(\dfrac{1}{P}\right) + 26.0$

10) $R_p(CO) = -0.000391 \left(\dfrac{1}{P}\right) + .0193$

For the 600-second runs:

11) $- \dfrac{1}{R_p(O_2)} = 0.236 \left(\dfrac{1}{P}\right) + 6.65$

12) $- R_p(O_2) = -.00287 \left(\dfrac{1}{P}\right) + .1426$

13) $\dfrac{1}{R_p(CO_2)} = 0.664 \left(\dfrac{1}{P}\right) + 10.27$

14) $R_p(CO_2) = -.00174 \left(\dfrac{1}{P}\right) + .0819$

15) $\frac{1}{R_p}(CO) = -0.50 \left(\frac{1}{P}\right) + 57.3$

16) $R_p(CO) = 0.000181 \left(\frac{1}{P}\right) + .0177$

The R_p values are proportional to the quantum yields, and P is the mean oxygen pressure in mm. These equations are restated in the discussion (Chapter IV, Eqs. 55&60, 63-68) in terms of actual quantum yields and mean oxygen concentration in molecules per cubic centimeter.

It is observed that the limiting values of the R_p's at large oxygen pressure, predicted by equations of the form (1), tend to be greater than those predicted by equations of the form (3). In the case of the carbon monoxide yield and also of the carbon dioxide yield for the 900-second runs, this discrepancy is greater than would be expected from the scatter in the data. It is not known what significance, if any, is to be attributed to the disagreement.

The data on oxygen uptake for the 900-second runs were also fitted to a curve of form: $\frac{1}{R_p(O_2)} = a + b\left(\frac{1}{P}\right) + c\left(\frac{1}{P}\right)^2$. The curve found was

17) $\frac{1}{R_p(O_2)} = 6.68 + 0.521\left(\frac{1}{P}\right) - 0.0027 \left(\frac{1}{P}\right)^2$.

At the lowest pressure used, the contribution from the $\left(\frac{1}{P}\right)^2$ term was 15% of the total calculated value of 1/Q.

At the next lowest pressure, the contribution was only 3%, and it would, of course, be smaller at higher pressures. Therefore, we do not believe that the data warrant the inclusion of the $(\frac{1}{P})^2$ term.

Table III shows the composition of the CO_2 in the runs with added O_2^{18}. The carbon dioxide is mostly $CO^{16}O^{18}$. The fraction of $CO^{16}O^{16}$ and of $CO^{18}O^{18}$ decreases with increasing $I_a \cdot t$, with the decrease in $CO^{18}O^{18}$ much more marked. This implies that after the first few minutes of reaction, the rate of formation, $\frac{dCO^{18}O^{18}}{dt}$, of $CO^{18}O^{18}$ is very small.

IV DISCUSSION

This discussion will concern itself mainly with the primary process in the photoreaction of biacetyl with oxygen. However, a knowledge of the secondary processes is necessary in order to interpret the experimental results. The questions to be answered here by a discussion of the secondary processes are:

a) How much oxygen is consumed for each excited molecule of biacetyl which reacts?

b) How much carbon dioxide is produced?

c) How much carbon monoxide is produced? And especially,

d) How do these yields vary with conditions?

If the answers to these questions were known, the data on production of products could be interpreted in terms of disappearance of excited biacetyl.

Secondary Processes

The radicals which might be found in this system are: CH_3, CH_3O, CH_3O_2, CH_3CO, CH_3CO_2, CH_3CO_3, $CH_3COCOCH_2$ and their oxidation products, and possibly also CH_3COCO_2 and CH_3COCO_3 and their oxidation products. The purpose of the short review presented here is to attempt to find which reactions of these radicals are likely to be significant in the system studied, and to

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attempt to determine the magnitude of the product yields, per molecule of biacetyl destroyed, assuming various radical intermediates. It may thus be possible to find a range of possible product yields per primary photochemical act.

a) CH_3 - Even at the lowest oxygen pressures used here, most of the methyl radicals would be expected to disappear by:[42,54]

$$(1) \quad CH_3 + O_2(+M) = CH_3O_2 + M$$

or[9,38,54]

$$(2) \quad CH_3 + O_2 = CH_2O + OH$$
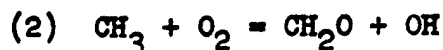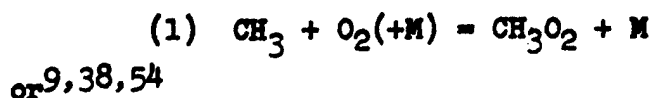
b) CH_3O_2 - These radicals probably react to form CH_3O by

$$(3) \quad 2CH_3O_2 = 2CH_3O + O_2$$
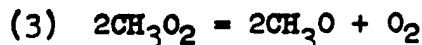
There is also a possibility of abstraction[30,81] to form methyl hydroperoxide.

$$(4) \quad CH_3O_2 + CH_3COCOCH_3 = CH_3O_2H + CH_3COCOCH_2$$
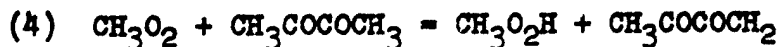
The corresponding reaction (4a) in azomethane photooxidation has been postulated by Shahin and Kutschke[81] to explain methyl hydroperoxide formation, but Subbaratnam and Calvert[95] found the hydroperoxide to be a minor product and explain its formation by (5).

$$(4a) \quad CH_3O_2 + CH_3N_2CH_3 = CH_3O_2H + CH_3N_2CH_2$$

$$(5) \quad CH_3O_2 + CH_3O = CH_3O_2H + CH_2O$$
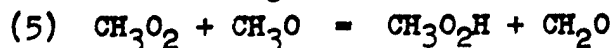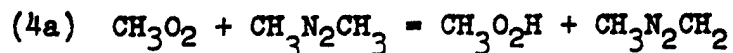
Reaction (4) will be neglected in the treatment to

follow.

Taylor and Blacet[96] propose

(6) $CH_3O_2 + O_2 = CH_3O + O_3$
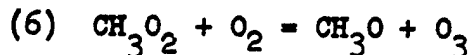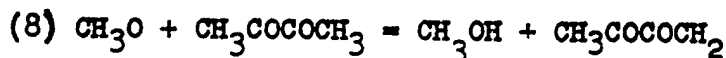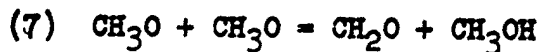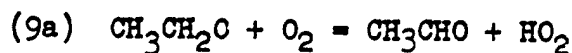
to explain the ozone formation observed by Haagen-Smit et al.[33] Reaction (6) is probably very endothermic, and will be disregarded in the rest of the discussion.

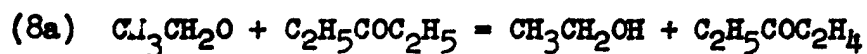c) CH_3O - Some of the reactions which can be proposed for this radical are

(7) $CH_3O + CH_3O = CH_2O + CH_3OH$

(8) $CH_3O + CH_3COCOCH_3 = CH_3OH + CH_3COCOCH_2$

(9) $CH_3O + O_2 = CH_2O + HO_2$

(10) $CH_3O + CH_3O = CH_3OOCH_3$
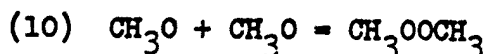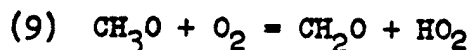
Dever and Calvert[24], from their study of azomethane oxidation, estimate $k_7/k_{10} > 60$. However, Heicklen and Johnston[38] estimate $k_7/k_{10} = 9.5$. In either case, more than 90% of the reaction second order in methoxy radicals is reaction (7).
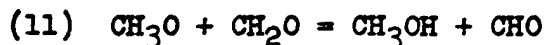
Reaction (9), proposed by Taylor and Blacet[96] is analogous to (9a), proposed by Jolley[45] in the photo-oxidation of diethyl ketone.
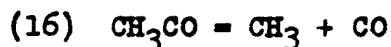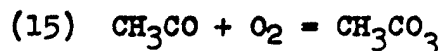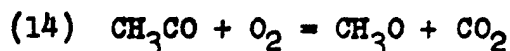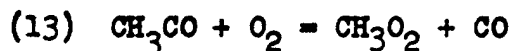
(9a) $CH_3CH_2O + O_2 = CH_3CHO + HO_2$

Jolley finds $k_{9a}/k_{8a} = 10 \pm 5$.

(8a) $CH_3CH_2O + C_2H_5COC_2H_5 = CH_3CH_2OH + C_2H_5COC_2H_4$

Also, if formaldehyde accumulates in the system, reaction (11) may be expected to occur.

(11) $CH_3O + CH_2O = CH_3OH + CHO$

d) CH_3CO - At room temperature, reaction (12) would not compete effectively with reactions (13)-(16).

(12) $CH_3CO + CH_3COCOCH_3 = CH_3CHO + CH_3COCOCH_2$

(13) $CH_3CO + O_2 = CH_3O_2 + CO$

(14) $CH_3CO + O_2 = CH_3O + CO_2$

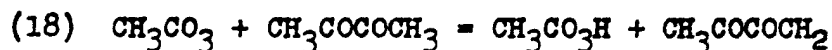(15) $CH_3CO + O_2 = CH_3CO_3$

(16) $CH_3CO = CH_3 + CO$

e) CH_3CO_2 - In the photolysis of methyl acetate, Wijnen[101,102] finds that this radical, if formed at all, decomposes by (17).

(17) $CH_3CO_2 = CH_3 + CO_2$
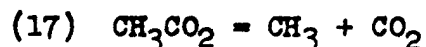
f) CH_3CO_3 - Peroxyacetic acid has been found as a product of the photo-oxidation of acetaldehyde,[20,60] and its presence explained by reaction (18a).

(18a) $CH_3CO_3 + CH_3CHO = CH_3CO_3H + CH_3CO$

By analogy, reaction (18) can be postulated.

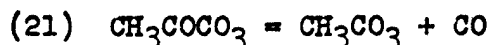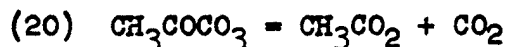(18) $CH_3CO_3 + CH_3COCOCH_3 = CH_3CO_3H + CH_3COCOCH_2$

Reaction (18) would be expected to be slower than (18a).

The radical CH_3CO_3 could also be an intermediate in reactions (13) and (14).

g) CH_3COCO_2 - By analogy with CH_3CO_2, it is suggested that this radical, if formed, decomposes by reaction (19):

(19) $CH_3COCO_2 = CH_3CO + CO_2$
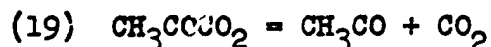
h) CH_3COCO_3 - By analogy with CH_3CO_3, reactions (20-22) are postulated for this radical, if it exists.

(20) $CH_3COCO_3 = CH_3CO_2 + CO_2$

(21) $CH_3COCO_3 = CH_3CO_3 + CO$

(22) $CH_3COCO_3 + CH_3COCOCH_3 = CH_3COCO_3H + CH_3COCOCH_2$

Before considering the reactions of the $CH_3COCOCH_2$ radical, some discussion of the reactions (4), (8), (18) and (22), which lead to its formation, will be presented. It will be noted that these reactions, together with reasonable reactions of the $CH_3COCOCH_2$ radical, imply a radical chain. Therefore, more information on the abstraction reactions is desirable.
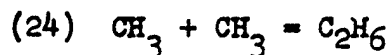
Apparently, the only reaction involving abstraction from biacetyl which has been studied is[5,12,14,15] (23):

(23) $CH_3 + CH_3COCOCH_3 = CH_4 + CH_3COCOCH_2$
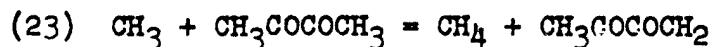
Comparing this reaction with (24), both Ausloos and Steacie[5] and Bell and Blacet[12] find

$$k_{23}/k_{24}^{1/2} = 10^{-13.0} - 10^{-13.2} \text{ at } 25°C.$$

$$(24) \quad CH_3 + CH_3 = C_2H_6$$

However, Ausloos and Steacie give $E_{23} = 8.5$ kcal. while Bell and Blacet give $E_{23} = 7.7$ kcal. The Ausloos-Steacie E_{23} is based primarily on data obtained at higher temperatures, and agrees well with the value obtained by the same workers using methyl radicals generated by (25).
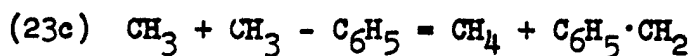
$$(25) \quad CH_3N_2CH_3 + h\nu = 2CH_3 + N_2$$
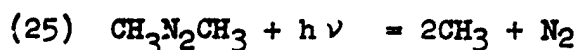
A rough extrapolation of the plots in Figure 1 of Reference 5 gives $\dfrac{A_{23}}{A_{24}^{1/2}} = 1 \times 10^{-7}$ (cm.^{3}/mol.sec.)$^{1/2}$ for the Ausloos-Steacie E_{23} and $\dfrac{A_{23}}{A_{24}^{1/2}} = 3 \times 10^{-8}$ (cm.^{3}/molecule sec.)$^{1/2}$ for the Bell-Blacet E_{23}. These are comparable to the following ratios calculated from Steacie's book[90]:

$$\frac{A_{23a}}{A_{24}^{1/2}} = 4 \times 10^{-8} \text{ (cm.}^3\text{/molecule sec.)}^{1/2}$$

$$A_{23b}/A_{24}^{1/2} = 8 \times 10^{-8}$$

$$A_{23c}/A_{24}^{1/2} = 3 \times 10^{-8}$$

(23a) $CH_3 + C_2H_6 = CH_4 + C_2H_5$

(23b) $CH_3 + CH_3COCH_3 = CH_4 + CH_3COCH_2$

(23c) $CH_3 + CH_3 - C_6H_5 = CH_4 + C_6H_5 \cdot CH_2$
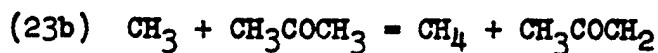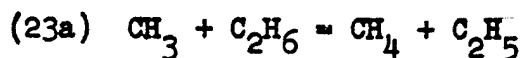
Thus all of the A-factors, A_{23}, A_{23a}-A_{23c}, are of the same order of magnitude. The activation energy for abstraction from biacetyl is lower than the activation energy for abstraction from acetone ($E_{23b} = 9.6$ kcal.) but is not unreasonable.

If k_{24} is taken[29,84] as 0.4×10^{-10} ($cm.^3$/molecule sec.) independent of temperature, one obtains as an estimade of the frequency factor for reaction (23) (23a-23c)

$A \cong 10^{-13}$ $cm.^3$ molecule^{-1} sec.$^{-1}$

It is desired to compare the known abstraction reactions of the methyl radical with those of the methoxy radical. Relations are sought which may be extended to the case at hand in which the rate of the abstraction by methyl is known, and the rate of abstraction by methoxy (and other radicals) is not. The available data on rates of abstraction by methyl are extensive but the corresponding data on methoxy are much less so.

Trotman-Dickenson and coworkers[13,80] have studied the reactions of methoxy radicals with a number of hydrocarbons. Table IV, comparing the activation energies and frequency factors for these reactions[13] and those for

the corresponding reactions of methyl,[90]
is given below. The reactions are written, in general, as

$$R + R'H = RH + R'$$

It can be seen that the A-factors for these abstractions by methyl are in good agreement with the approximate value, 10^{-13} cm.^{3} molecule^{-1} sec.$^{-1}$.

Writing the general reactions:

(23d) $CH_3 + HR' = CH_4 + R'$

(8b) $CH_3O + HR' = CH_3OH + R'$
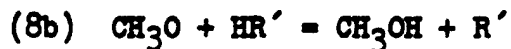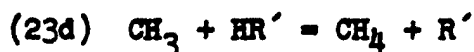
it is seen from the table that, to a very rough approximation,

$$A_{8b}/A_{23d} = 10^{0.8}$$

$$E_{8b}-E_{23d} = -3 \text{ kcal.}$$

It appears that some of the error introduced in these approximations will cancel, since when A_{8b}/A_{23d} is high, $E_{8b}-E_{23d}$ is low. Nevertheless, the rate constants derived using these expressions are not expected to be very accurate.

At 27°C, $e^{3000/RT} = 10^{2.2}$, therefore $k_{8b}/k_{23d} = 10^3$.

Thus $k_8/k_{24}^{1/2} \sim 10^{-10}$, and combining this with Gomer and Kistiakowsky's[29] value of k_{24}, one obtains:

$$k_8 \sim 10^{-15} \text{ cm.}^3/\text{molecule second.}$$

TABLE IV

Comparison of Rates of Abstraction by Methyl and by Methoxy Radicals[13,90]

	E_a		$E_a(CH_3) -$
	$R=CH_3O$	$R=CH_3$	$E_a(CH_3O)$
$R'H$ = Ethane	7.1 kcal.	10.4	3.3
n-Butane	2.9	8.3	5.4
iso-Butane	4.1	7.6	3.5
neo-Pentane	7.3	10.0	2.7
cyclopropane	9.7	10.3	0.6
methyl acetate*	7.1	10.	2.9

	$\log_{10}A$	(A in $cm.^3 molecule^{-1}sec.^{-1}$)	
			$\log_{10}\left(\dfrac{A_{CH_3O}}{A_{CH_3}}\right)$
$R'H$ = Ethane	-12.0	-12.8	0.8
n-Butane	-13.0	-13.0	0.0
iso-Butane	-12.5	-13.1	0.6
neo-Pentane	-11.7	-12.7	1.0
cyclopropane	-11.3	-13.1	1.8

---

* Data from Wijnen[101] interpreted by Shaw and Trotman-Dickenson[80]

Next, an attempt is made to estimate k_7, in order to determine whether the metathesis or the abstraction is the predominant reaction of the methoxy radical under the conditions used in the present work.

Wijnen, from his study of the photolysis of methyl-d_3 acetate, CH_3COOCD_3,[102] estimates at 30°C and at 90°

$$(26) \quad k_{24}k_{7a}/k_{27}^2 = 11$$

$$(7a) \quad 2CD_3O = CD_3OD + CD_2O$$

$$(27) \quad CH_3 + CD_3O = CH_3OCD_3$$
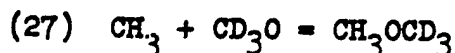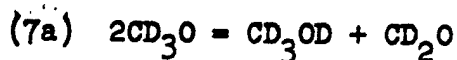
He also gives $k_{28}/k_{27} = 1.4$ at 30° and at 90°C.

$$(28) \quad CH_3 + CD_3O = CH_3D + CH_2O$$
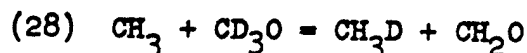
Substitution of $k_{24} = 0.4 \times 10^{-10}$ into Eq. (26) leads to

$$(29) \quad k_{7a}/k_{27}^2 = 3 \times 10^{11} \text{ (cm.}^3/\text{molecule sec.)}^{-1}$$

From the preceding argument about the relative rates of abstraction by methyl and by methoxy radicals, one expects $k_{7a} > k_{28}$. But since $k_{28} = 1.4\ k_{27}$, $k_{7a} > 1.4\ k_{27}$. Thus, by setting $k_{8a} = 1.4\ k_{27}$ in expression (29), one obtains an estimated minimum value of k_{7a}. This value is 0.6×10^{-11} cm.^{3}/molecule second, which is not unreasonable.

(Had k_{28} been set equal to 10^{-3} k_{7a}, as suggested on page 48, the exceedingly high value of 0.3×10^{-5} cm.^{3}/molecule second would have been obtained for k_{8b}, and 0.3×10^{-8} cm.^{3}/molecule second for k_{28}. However, this would have been a considerable over-extension of the correlation which led to the ratio 10^3 (cf. pages 47-48) for the following reasons:

    (a) The activation energy for reactions (7a) and (28) is approximately zero. This is seen from the constancy of the ratios found by Wijnen with temperature, and the probable near-zero activation energies for the radical association reactions (24) and (27).

    (b) The frequency factor cannot be much greater than the number of collisions calculated using reasonable cross sections. This number is of the order of 10^{-10} cm.^{3}/molecule second.)

The collision number gives a maximum value of k_{8b}. Thus an estimate of k_{7a} is $10^{-11} \leqslant k_{7a} \nleqslant 10^{-10}$ cm.^{3}/molecule second. Reaction (7a) is thus seen to be a very efficient reaction.

A check of some sort may be had on the estimate of k_{7a}. Placing the value obtained above for k_{7a} into expression (29), one obtains $k_{27} = 10^{-11}$ to within a factor of two. Bercés and Trotman-Dickenson[13] have estimated k_{27a} by methods quite distinct from those used

here, and obtained log k_{27a} = -10.3 or -9.2.

(27a) $CH_3 + CH_3O = CH_3OCH_3$
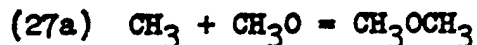
They consider the value -10.3 to be more reliable. Thus, their k_{27a} differs from the present k_{27} by about one order of magnitude. (The results in Table IV quoted from Bercés and Trotman-Dickenson are calculated (by them) using log k_{27a} = -10.3. They were not recalculated here as there seems no compelling reason to favor one estimate over the other.)

Reactions (27a) and (27) should have approximately equal rate constants, and reaction (7a) should be no faster than (7). The primary isotope effect should favor (7) over (7a), but this effect is small for reasons similar to those given on page 51 . Therefore k_7 will be assumed to be equal to k_{7a}.

Having estimated the rate constants,

$k_8 \sim 10^{-15}$ cm.^{3}/molecule second

$$10^{-11} \leqslant k_7 \leq 10^{-10} ,$$

one can attempt to estimate the relative importance of reactions (7) and (8). For simplicity, one assumes that these are the only reactions which destroy methoxy radicals. Then the steady-state equation in these radicals is

(30) $0 = R_M - 10^{-15}\left[CH_3O\right]\left[B\right] - 10^{-10}\left[CH_3O\right]^2 ,$

where R_M is the rate of formation of methoxy radicals and $[B]$ is the biacetyl concentration.

Setting $R_M = I_a \sim 10^{13}$ cm.$^{-3}$ sec.$^{-1}$, and $[B] = 10^{18}$ molecule/cm.^{3}, Eq. (30) becomes

$$0 = 10^{13} - 10^3 [CH_3O] - 10^{-10} [CH_3O]^2$$

Solution of this equation gives

$$[CH_3O] \sim 10^{10}.$$

Now, the ratio of the rate of abstraction to the rate of disproportionation is

$$\frac{10^{-15} [CH_3O] [B]}{10^{-10} [CH_3O]^2}$$

which is $\sim 10^3$. The implication of this calculation is that far more methoxy radicals react by abstraction than by disproportionation. If methoxy radicals are formed in the system, then the possibility of a chain reaction cannot be ignored.

1) $CH_3COCOCH_2$ - Taylor and Blacet[96] propose

(31) $CH_3COCOCH_2 + O_2 = CH_3CO + CO_2 + CH_2O$.
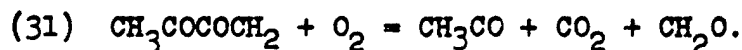
If this be followed by (13), (14) or (15), a radical chain is seen to occur.

The near-constancy of quantum yields over the hundredfold variation in light intensity used in the

present work implies that the major chain-terminating step is first-order in a chain carrier (free radical). Reaction (9) fits this qualification, if one makes the usual assumption[98] that the HO_2 radical formed is inert in the system at room temperature. An alternative reaction is (32).

(32) R + wall = ?

That is, perhaps some radicals, R, recombine on the walls with adsorption the rate-determining step. This reaction may be construed as a reason for the large scatter in experimental results found in this investigation, and others[73,96] of this system. Specifically, Taylor and Blacet[96] found that their results depended on the previous conditioning of the cell wall.

If the chain mechanism does indeed predominate, then for each excited biacetyl molecule which is destroyed, several normal biacetyl molecules also react. Thus, unless the chain length be known, the questions originally proposed (page 41) regarding the amounts of products formed cannot be answered. In addition, the problem of variation of yields with conditions can not easily be answered. However, this latter problem is crucial to the interpretation of the data. It will be assumed, in the following discussion of the primary process, that the radicals formed in the primary process

undergo the same sequence of reactions over the whole range of variables studied in this work. It is emphasized here that this is an essential assumption upon which the succeeding discussion depends, and that this assumption, though consistent with the available data, is not based on any experimental evidence.

The measurements with O_2^{18} show that, except at the early stages, almost all the CO_2 comes from the carbonyl carbon atom. The implication of a comparison of the results of the long and short runs is that the nature of the reaction undergoes a change as some product builds up in the system (or some impurity is destroyed). Some limit on the possible concentration of products is obtained by noting that in 10 minutes approximately .02 mm. O_2 are used up at the higher oxygen pressure. The change of rates of product formation with time is not uncommon in oxidation reactions.[18,100] Formaldehyde has been postulated as a cause, with reaction (11) the key reaction. This implies that the rate of (11) is about 10^3 k_8. However, the corresponding abstractions by methyl differ only by about one order of magnitude at room temperature.[16,99] Some other product would seem to be responsible. If HO_2 is as inert as believed, it might be present in sufficient quantity to affect the course of reaction. This is not established, however.

The Primary Process

The discussion of the primary process will be divided into two parts: the first will assume that the relation between the quantum yields of products, ϕ_P, and the concentration of oxygen, $[O_2]$, is given by Eq. (33); and the second that the relation is Eq. (34) (cf. Chapter III).

(33) $1/\phi_P = a + b/[O_2]$

(34) $\phi_P = a' - b'/[O_2]$

First, a general discussion will be given, of the primary process in biacetyl. The steps necessary for biacetyl at 4358 Å without oxygen are:[63]

(35) $B + h\nu = {}^1B$

(36) ${}^1B = D$

(37) ${}^1B = B$

(38) ${}^1B = {}^3B_m$

(39) ${}^1B = B + h\nu_f$

(40) ${}^3B_m = D$

(41) $= B$

(42) $= {}^3B_o$

(43) ${}^3B_o = D$

(44) $= B$

(45) $= B + h\nu_p$

(46) ${}^3B_o + {}^3B_o = D + B$
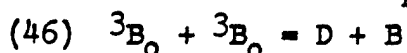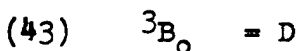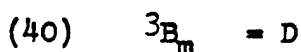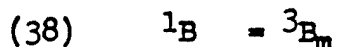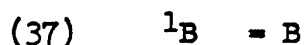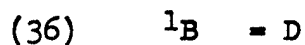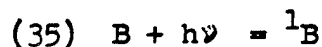
In Eqs. (35-46) D represents decomposition, B ground-state biacetyl, ^{1}B biacetyl in its first excited singlet state, ^{3}B biacetyl in its first excited triplet state, the subscript m refers to vibrational excitation, and sub-script zero to lack of vibrational excitation, $h\nu_f$ represents fluorescence, and $h\nu_p$, phosphorescence. The steps (35-45) are kinetically first-order in the pressure range used. At room temperature, the dissociation steps, (36), (40) and (43) are not important.[82]

With regard to the reaction of oxygen with biacetyl, Groh[32] has shown that oxygen does not affect the fluorescence, $h\nu_f$. Therefore no reaction of oxygen with ^{1}B need be considered, as these would reduce the fluorescence efficiency. Thus, the extra reactions to consider in this system are:

$$(47) \quad ^3B_m + O_2 = P$$

$$(48) \quad ^3B_m + O_2 = B + O_2$$

$$(49) \quad ^3B_o + O_2 = P$$

$$(50) \quad ^3B_o + O_2 = B + O_2$$
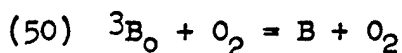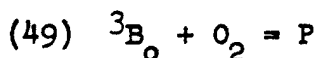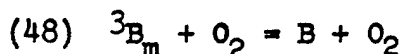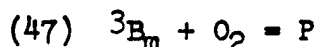
Also, since oxygen reduces the concentration of ^{3}B, reaction (46) can be neglected. (In Eqs. (47) and (49), P represents products of reaction.)

This mechanism, steps (35-45) and (47-50), leads

to the expressions (51-53) for $[^3B_o]$ Q_p, the phosphorescence efficiency, and γ_p, the lifetime of phosphorescence.

(51)
$$[^3B_o] = \frac{k_{38}k_{42} \, (k_{36}+k_{37}+k_{38}+k_{39})^{-1} \, I_a}{\left\{k_{43}+k_{44}+k_{45}+(k_{49}+k_{50}) \, [O_2]\right\}\left\{k_{40}+k_{41}+k_{42}+(k_{47}+k_{48}) \, [O_2]\right\}}$$

(52)
$$\gamma_p = \frac{1}{(k_{49}+k_{50}) \, [O_2] + k_{33}+k_{34}+k_{35}}$$

(53)
$$Q_p = \frac{k_{45}k_{38}k_{42} \, (k_{36}+k_{37}+k_{38}+k_{39})^{-1} \, \gamma_p}{k_{40}+k_{41}+k_{42}+ (k_{47}+k_{48}) \, [O_2]}$$

Comparison of Eqs. (51) and (52) shows that the quenching constant calculated from measurements of Q_p should be somewhat greater than that calculated from measurements of γ_p. Also, the graph of Q_p vs. $[O_2]$ should not follow a strict Stern-Volmer[91] plot. If $k_{47} + k_{48} \ll k_{40} + k_{41} + k_{42}$, however, the quenching constants should be identical, and the graph of $\frac{1}{Q_p}$ vs. $[O_2]$ should be linear. In fact, the quenching constant*

---

* The values are 1.5, 1.3 and 2.4 x 10^{-15} cm.^{3}/molecule in the order named. The quenching constant is defined as k in Q_o/Q or $\gamma_o/\gamma = 1 + k \, [O_2]$.

calculated by Kaskan and Duncan[47] from studies of the lifetime agrees well with that calculated from Coward and Noyes[23] or Almy, Fuller and Kinzer[3], who studied the decline of phosphorescence yield with oxygen pressure. Therefore, steps (47) and (48) will be disregarded in the following discussion. Now, a considerable simplification can be obtained by writing

$$[^3B_o] = I_a \phi_t \gamma \ ,$$

where ϕ_t is the quantum yield of formation of $[^3B_o]$. In this equation, only γ is dependent on $[O_2]$. To shorten the expression (52) for γ one can write:

$$k_b = k_{49} + k_{50}$$

$$k_u = k_{33} + k_{34} + k_{35}$$

$$\gamma = (k_u + k_b [O_2])^{-1} \ .$$

The primary yield of reaction is given by $k_{49} [^3B_o] [O_2] / I_a$ or:

$$\phi_P = \frac{k_{49}[O_2] \phi_t}{k_u + k_b [O_2]}$$

$$(54) \quad \frac{1}{\phi_P} = \frac{k_b}{k_{49} \phi_t} + \frac{k_u}{k_{49} \phi_t} \frac{1}{[O_2]}$$

First Part: Relation (54) for the primary reaction yield is of the same form as relation (33) for the

product yields. The assumption made on page 55 is now brought into play. It is assumed that:

$$-\bar{\phi}_{O_2} = n\phi_P$$

$$\bar{\phi}_{CO_2} = m\phi_P$$

$$\bar{\phi}_{CO} = r\phi_P$$

One check on this assumption is that the ratio of slope to intercept for the experimentally determined equations of form (33) should be k_u / k_b, which is the reciprocal of the quenching constant (cf. footnote p.58). The equations of this form, Eqs. (III-5,7,9,11,13,15),* are reproduced, with $[O_2]$ in molecules/cm.[3], and ϕ the experimentally determined quantum yield, as Eqs. (55-60).

(55) $\quad \bar{\phi}_{O_2}^{-1} = 0.58 \times 10^{16}[O_2]^{-1} + 3.3$

(56) $\quad \phi_{CO_2}^{-1} = 1.05 \times 10^{16}[O_2]^{-1} + 4.1$

(57) $\quad \bar{\phi}_{CO}^{-1} = 0.55 \times 10^{16}[O_2]^{-1} + 11.$

(58) $\quad \phi_{O_2}^{-1} = 0.33 \times 10^{16}[O_2]^{-1} + 2.9$

(59) $\quad \bar{\phi}_{CO_2}^{-1} = 0.93 \times 10^{16}[O_2]^{-1} + 4.6$

---

* Equation (III-1) refers to Eq. (1) of Chapter III, etc.
Equation (1) refers to Eq. (1) of this chapter.

$$(60) \quad \phi_{CO}^{-1} = 0.70 \times 10^{16} [O_2]^{-1} + 25$$

Equations (55-57) refer to the results of the 900-second runs, and (58-60) to the results of the 600-second runs. The slope-to-intercept ratios of these equations are, respectively, 18, 25, 56, 11, 21, 2.8 x 10^{14} molecule/cm.^{3}. The reciprocal of 1.5 x 10^{-15} is 6.7 x 10^{14}. The agreement is not very bad. Incidentally, it is noted that, while the slope-to-intercept ratios for the equations involving oxygen uptake and carbon dioxide formation are in fair agreement with one another, the ratios for Eqs. (57) and (60) for carbon monoxide formation are quite different from these and from each other. The explanation for this discrepancy is not certain, but it is possible that the carbon-monoxide-forming reaction depends on time elapsed, i.e., a reaction like (11) may be followed by (61).

$$(61) \quad HCO + O_2 = CO + HO_2$$
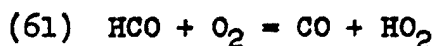
The intercepts of Eqs. (55-60) are given by relations like:

$$(62) \quad \frac{1}{\phi_{CO_2}(\infty)} = \frac{k_b}{m \, k_{49} \, \phi_t} \quad ,$$

where $\phi_{CO_2}(\infty)$ denotes the limiting quantum yield of carbon dioxide at high oxygen pressure. This expression

is the product of three unknown quantities: m, which is probably > 1; k_b/k_{49}, which is $\gg 1$; and ϕ_t, which obeys the inequalities $1 > \phi_t \gg 0.15$.[1]

It will be noted that the limiting values of the various ϕ's obtained in this work are smaller, by about a factor of six, than the ϕ's obtained by Porter.[73] The actinometry in the present work is not good (cf. Chapter II), but the discrepancy is greater than can easily be explained by experimental error. It is suggested that, on the hypothesis of a chain reaction, some of the difference may be due to different efficiencies of the chain-terminating step (32). Nevertheless, the discrepancy must be considered largely unexplained. The agreement of the slope-to-intercept ratios for this work with the ratios from phosphorescence data is independent of the absolute yields.

If one assumes that $k_{49} = k_b$, which is the assumption that all deactivation of triplet biacetyl by oxygen is by chemical reaction; and that $\phi_t = 0.15$, which is a minimum value, and substitutes these values, together with the experimentally determined $\overline{\phi}(\infty)$'s into expression (62) and its analogues, one obtains:

$$n = 2.0,\ 2.3$$
$$m = 1.6,\ 1.4$$
$$r = 0.6,\ 0.3\ .$$

The first figure quoted in each line represents the results of the 900-second runs; the second, those of the 600-second runs. These values are quite small, which means that the reaction chains are very short. Larger values of ϕ_t would imply a shorter chain length, while if $k_b > k_{49}$, a longer chain length would be inferred from the data.

An estimate of ϕ_t has been made by Bäckström and Sandros.[8] (ϕ_t, as defined on page 59, is the quantum yield of ^3B_o. It is necessarily equal to, or less than, the total quantum yield of triplet biacetyl. The ratio between these yields is $\dfrac{k_{42}}{k_{41} + k_{42}}$.

Bäckström and Sandros[8] find that the phosphorescence yield in benzene solution for biacetyl directly photo-excited is equal to that for biacetyl phosphorescence sensitized by benzophenone (when the biacetyl concentration is high enough for maximum energy transfer from benzophenone). They find that the sensitized emission is pure phosphorescence. Therefore, they conclude that the efficiency of formation of triplet biacetyl from the singlet is near unity, i.e., $k_{38} \gg k_{37} + k_{39}$. However, they note that "since the phosphorescence lifetime of biacetyl in the vapor state at 25°C has been found[47] to be 1.80×10^{-3} second, whereas the natural lifetime may be assumed[59] to be about 2.25×10^{-3} second,

the phosphorescence yield observed by Almy and Gillette corresponds to a conversion efficiency of only about 20%." (The value quoted for the natural lifetime is the lifetime measured by McClure[59] in E.P.A. at 77°K.) Thus Bäckström and Sandros conclude that $\phi_t = 0.20$. Ishikawa and Noyes[43,44] have found that the ratio of biacetyl phosphorescing to biacetyl excited for the emission sensitized in the gas phase by benzene is 0.15, which is the same as that found by Almy for the unsensitized emission. Thus the argument of Bäckström and Sandros holds equally well for the vapor. The present results, though somewhat low, are consistent with $\phi_t = 0.20$. Unfortunately, the interpretation to be placed on the present data is by no means clear. In any case, this work does not yield any information on the efficiency of formation of triplet biacetyl, as distinct from ϕ_t.

Bäckström and Sandros suggest that the cause of the discrepancy between the yield of triplet biacetyl and ϕ_t is internal conversion from the higher vibrational levels of the triplet to the ground state, step (41) in the mechanism stated here. If this is the correct explanation, this step must be fast enough to compete with collisional deactivation (step (42),which is written as first order). No data are available concerning this

point. However, the explanation of Bäckström and Sandros does not seem unreasonable.

Hammond has suggested an alternate explanation involving the formation of two triplet states, one of which does not phosphoresce or, if the present work is correct, react with oxygen. This also explains the data. In fact, Sidman and McClure[85,86] find a singlet-triplet absorption originating from 20,421 cm.$^{-1}$ (4900 Å) which they assign to a $^3A_u \leftarrow {}^1A_g$ transition. They find no corresponding emission. It is conceivable that this ^3A_u state is the inactive triplet suggested by Hammond. However, there is no evidence for its formation from the singlet.

It is not possible to choose between the two alternate explanations at the present time.

Second Part: No mechanism is seen by the present author which wo   a relation of form (34) and not of form (33). Of   .e, (34) is an approximation at high pressure to (33).

$$(33) \quad \frac{1}{\varphi_P} = a + \frac{b}{[O_2]}$$

Equation (33) can be inverted to give

$$\varphi_P = \frac{1}{a + \frac{b}{[O_2]}} \simeq \frac{1}{a}\left(1 - \frac{b/a}{[O_2]}\right)$$

which is of the form (34) with $a' = \frac{1}{a}$, $b' = \frac{b}{a^2}$. It is not understood why the approximation should fit the data better than the original expression.

It is interesting to note that the only case in which expression (34) fits the data much better than (33) is that of the carbon monoxide yield (cf. Ch. III), and that carbon monoxide yield, plotted according to (33) gives anomalous results (page 61).

Nevertheless, Eqs. (III-6,8,10,12,14,16) are reproduced here, with $[O_2]$ in molecules/cm.^{3} as (63-68).

900-second runs:

(63) $\not\!\phi_{O_2}$ = -1.5 x 10^{14}($\frac{1}{[O_2]}$) + 0.26

(64) $\not\!\phi_{CO_2}$ = -1.1 x 10^{14}($\frac{1}{[O_2]}$) + 0.18

(65) $\not\!\phi_{CO}$ = -0.28 x 10^{14} ($\frac{1}{[O_2]}$) + 0.043

600-second runs:

(66) $\not\!\phi_{O_2}$ = -2.1 x 10^{14} ($\frac{1}{[O_2]}$) + 0.32

(67) $\not\!\phi_{CO_2}$ = -1.3 x 10^{14} ($\frac{1}{[O_2]}$) + 0.18

(68) $\not\!\phi_{CO}$ = -0.13 x 10^{14} ($\frac{1}{[O_2]}$) + 0.040

Stoichiometry of the overall reaction - The ratio of the limiting oxygen uptake to the carbon dioxide yield is 1.5 $\pm$ 0.3 (the ratios are 1.24, 1.58, 1.44, 1.78 for Eqs.

(55) and (56), (58) and (59), (63) and (64), and (66) and (67), respectively). The ratio of the limiting oxygen uptake to the sum of carbon dioxide and carbon monoxide is 1.2 ± 0.3 (0.9, 1.3, 1.2, 1.4 in the same order). Therefore if the carbonyl groups of the reacting biacetyl all give carbon dioxide, and no carbon monoxide, using one oxygen atom ($= 0.5$ oxygen molecule) from the molecular oxygen, then the methyl portion of the biacetyl uses 1.0 ± 0.3 oxygen molecule per methyl group. On the other hand, if all the carbon monoxide comes from the carbonyl portion, then these groups use only 0.8 atom of oxygen per group, and the methyl group uses 1.1 ± 0.3 molecule oxygen per methyl.

It seems likely that the true value of oxygen uptake per methyl group lies between the two values calculated above, although Taylor and Blacet's[96] work suggests that most of the carbon monoxide comes from the carbonyl group at 3130 Å.

The two extremes yield the following stoichiometric equations:

(69) $\quad C_4H_6O_2 + 3O_2 = 2CO_2 + 0.5CO + X$

(70) $\quad C_4H_6O_2 + 2.4O_2 = 1.6CO_2 + 0.4CO + Y,$
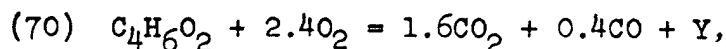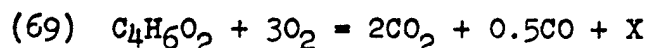
where X is a group of undetermined compounds of C:H:O ratio 1.5:6:3.5, and Y is a group of compounds of C:H:O

ratio 2:6:3.2. Neither of these ratios can be explained on the basis of the products CH_3OH, CH_2O, H_2O; but they need a more highly oxygenated compound also, e.g. formic or acetic acid. Of course, if acetic acid is formed in appreciable quantities, Eqs. (69) or (70) should have more than one biacetyl on the left-hand side.

Many mechanisms could be written which fit the data. For example, if one takes the mechanism proposed by Taylor and Blacet[96] and assumes that the chain-terminating steps second order in free radicals are negligible, and substitutes a primary process of form (49), e.g. (49a), and disregards the ozone-forming steps, one obtains a mechanism which can give the correct oxygen-pressure and intensity dependence. However, because of the lack of data concerning liquid products, the writing of a detailed mechanism at the present time would be a pointless exercise.

(49a) $^3B_0 + O_2 = 2CH_3 + 2CO_2$
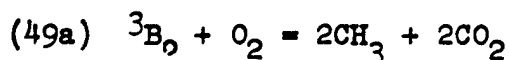
Some thirty possible secondary steps have been proposed in this discussion, and very few eliminated. To choose among these steps on the basis of the present data would be exceedingly speculative (but cf. Heicklen and Johnston[38]). However, it seems fairly well established that the reactants in the primary process are thermally equilibrated triplet biacetyl and oxygen.

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